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(54) **Detergent powders containing silicones**

(57) A process for the preparation of a pulverulent detergent with improved solution properties for use in washing machines, containing an organic silicon polymer as foam inhibitor, in which (A) a powder which has been spray dried using hot gases, and which contains at least one anionic and/or non-ionic active substance and

at least one structural substance, (B) a pulverulent or granular premix prepared by granulating one or more structural substances and/or magnesium silicate with an organic silicon polymer and (C) a second pulverulent or granular premix prepared by granulating a pulverulent per-compound and/or one or more structural substances with at least one non-ionic active substance which contains polyglycol ether groups, are mixed together.

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## SPECIFICATION

Process for the Preparation of Pulverulent Detergents with Improved Solution Properties,  
Containing Organic Silicon Polymers

Detergents which contain from inhibiting organic silicon polymers, hereinafter briefly referred to as "silicones", are well known. It has already been proposed that the silicones used in the production of washing powder should not be added to the aqueous slurry which is dried by hot spraying but should be subsequently incorporated in the finished washing powder, because the spray drying process in many cases reduces the foam inhibiting action of the silicones. On the other hand, considerable practical difficulties are encountered in achieving sufficiently uniform distribution of the small quantities of silicones required for foam inhibition in the comparatively large quantity of powder to ensure reproducible results. These difficulties can be overcome by first applying the silicones to carrier substances and then mixing this premix to the other powder components.

Although uniform distribution of the foam inhibitor in the powder is thereby obtained, it is in practice found that the silicones deleteriously affect the wetting characteristics of the powder mixture. The washing powder is wetted more easily, so that when introduced into the powder dispenser of a domestic washing machine it becomes completely soaked with water as soon as the water is turned on, and forms a more or less compact paste. This paste dissolves only very slowly on further addition of water, so that considerable residues are left in the dispenser and the outflow pipes at the end of the washing-in process and form solid deposits in the course of time.

A process has now been found which reduces or substantially obviates these disadvantages. The invention relates to a process for the preparation of pulverulent detergents with improved solution properties, containing organic silicon polymers as foam inhibitors, by mixing three powder constituents, characterised in that

A) 1 part by weight of a powder which is free from organic silicon polymers and per-compounds and has been spray dried using hot gases and contains

5 to 30% by weight of at least one anionic and/or non-ionic active substance;  
50 to 94% by weight of at least one structural substance which is a phosphate, polyphosphate, silicate, aluminosilicate, carbonate, sulphate, polycarboxylate or phosphate in the form of its alkali metal salt; and

1 to 20% by weight of other conventional detergent constituents;

B) 0.01 to 0.5 parts by weight of a pulverulent or granular premix prepared by granulating one or more of the structural substances mentioned under (A) with from 1 to 10% by weight, based on the premix, of organic silicon polymers, and

C) 0.05 to 1 part by weight of another pulverulent or granular premix prepared by granulating pulverulent per-compound and/or one or more of the structural substances mentioned under (A) with 3 to 25% by weight, based on the weight of the premix, of at least one non-ionic active substance

containing polyglycol ether groups, which active substance consists to an extent of at least 40% by weight of a compound having from 12 to 22 carbon atoms in the hydrophobic residue and in which the proportion of the number of ethylene glycol ether groups to the number of carbon atoms in the hydrophobic residue is in the range of from 1:3 to 1:6 are mixed together so that the total quantity of organic silicon polymers in the mixture is from 0.05 to 1.6% by weight and the total quantity of non-ionic active substance which has the ratio of from 1:3 to 1:6 is 1 to 10% by weight.

Powder component (A) is obtainable in known manner by the spray drying of aqueous generally containing from 50 to 30% by weight of water by means of a current of hot gases, in particular air, i.e. gases heated to temperatures of from 200°C to 320°C.

The constituents of component (A) comprise from 5 to 30% by weight, preferably from 10 to 25% by weight of surface active agents as active washing constituents, from 50 to 94% by weight, preferably from 60 to 89% by weight of structural components, and from 1 to 20% by weight, preferably from 2 to 20% by weight of other conventional constituents of detergents but no silicones and no per-compounds or bleaching agents containing active chlorine, and no bleaching activators, enzymes or other substances which are unstable under hot spray drying conditions. Anionic surface active agents suitable for the preparation of component (A) include those of the sulphonate or sulphate type, in particular alkylbenzene sulphonates, olefine sulphonates, alkane sulphonates and  $\alpha$ -sulpho fatty acid esters, primary alkyl sulphates and the sulphates of ethoxylated higher molecular weight alcohols containing from 2 to 3 glycol ether groups. Alkali metal soaps of fatty acids of natural or synthetic origin are also suitable, e.g. the sodium soaps of coconut, palm kernel or tallow fatty acids and, if even greater from inhibiting is desired, alkali metal soaps of hydrogenated rape seed oil or fish oil fatty acids may also be used. The anionic surface active agents are preferably in the form of their sodium salts. If the above mentioned anionic and zwitterionic compounds contain an aliphatic hydrocarbon group, this should preferably be straight chained and have from 8 to 22, preferably from 12 to 18, carbon atoms. In compounds which contain an araliphatic hydrocarbon group, the unbranched alkyl chains preferably have from 6 to 16, more particularly from 10 to 14 carbon atoms.

The quantity of foam inhibiting silicones required varies according to the nature and quantity of

anionic surface active agents used and this must be taken into account when deciding on the composition of the individual components of the mixture. Compositions which are free from soap and those which contain a comparatively high proportion of powerful foaming agents, in particular alkane sulphonates, olefine sulphonates, alkyl sulphates and alkyl glycol ether sulphates, require larger quantities of silicones than those in which the surface active constituents mainly consist of alkyl benzene sulphonates and soaps or non-ionic surface active agents.

Suitable non-ionic surface active agents include in particular the ethoxylation products of saturated or monounsaturated aliphatic primary alcohols having from 12 to 24, preferably from 12 to 18 carbon atoms and from 3 to 20, in particular from 4 to 15 ethylene glycol ether groups. Suitable alcohols from which these ethoxylation products are derived include, for example, those of natural origin, such as coconut or tallow fatty alcohols or oleyl alcohol or also oxo alcohols or synthetic alcohols obtained by ethylene polymerisation.

Also to be included among suitable non-ionic surface active agents are the ethoxylation products of secondary alcohols and vicinal diols having from 12 to 18 carbon atoms and of alkyl phenols having from 6 to 12 carbon atoms in the alkyl group. The number of glycol ether groups should again be 3 to 20, preferably 4 to 15. The partial volatility of the non-ionic surface active agents under conditions of hot spray drying, which is shown by the formation of fumes, can be considerably reduced by partially or completely replacing the ethoxylated alcohols and alkyl phenols mentioned above by alcohols and alkyl phenols prepared in two stages, in which from 0.5 to 3 mol of propylene oxide per mol of starting compound is added in the first stage and the intended quantity of ethylene oxide is added only in the second stage.

The mixture may also contain non-ionic surface active agents which are derived from the compounds mentioned above but contain both ethylene glycol ether groups and propylene glycol ether groups in a different sequence, for example alcohols having from 10 to 30 ethylene glycol ether groups and from 3 to 30 propylene glycol ether groups. Ethoxylation products of mercaptans, fatty acid amides and fatty acids may also be present. Water-soluble polyethylene oxide adducts of polypropylene glycol, ethylene diaminopolypropyleneglycol or alkylpolypropylene glycol having from 1 to 10 carbon atoms in the alkyl chain, which adducts contain from 20 to 250 ethylene glycol ether groups and from 10 to 100 propylene glycol ether groups may also be used. The aforesaid compounds normally contain from 1 to 5 ethylene glycol units per propylene glycol unit. Non-ionic compounds such as aminoxides and sulfoxides may also be used, and these may also be ethoxylated.

Suitable structural substances include the polymer phosphates, carbonates, silicates and sulphates of potassium and, particularly, of sodium. The silicates contain a proportion of  $\text{SiO}_2$  to  $\text{Na}_2\text{O}$  in the range of from 1:1 to 3.5:1. A suitable polymer phosphate is, in particular, pentasodium triphosphate which may be present as a mixture with its products of hydrolysis, the mono and di-phosphates, and with more highly condensed phosphates, e.g. tetraphosphates. Aqueous aluminosilicates of potassium or, particularly, of sodium which are capable of cation exchange and correspond to the following general formula may also be used:  $(\text{Na}_2\text{O})_x \cdot \text{Al}_2\text{O}_3 \cdot (\text{SiO}_2)_y \cdot (\text{H}_2\text{O})_z$  wherein  $x=0.9-1.3$ ,  $y=1.3$  to  $4.0$  and  $z=1$  to  $6$ .

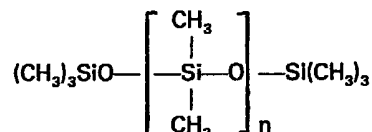
These aluminosilicates generally have a particle size of from  $0.1$  to  $20 \mu$  and are preferably crystalline.

The polycarboxylic acids used are mainly complex-forming aminopolycarboxylic acids. These include, in particular, the alkali metal salts of nitrilotriacetic acid and ethylene diaminetetracetic acid. The higher homologues of these aminopolycarboxylic acids are also suitable. Polycarboxylic acids which are free from nitrogen and from complex salts with calcium ions, including also polymers which contain carboxyl groups, are also suitable. Examples of such acids include citric acid, tartaric acid, benzene hexacarboxylic acid and tetrahydrofuran tetracarboxylic acid. Other suitable polycarboxylic acids include polycarboxylic acids containing carboxymethyl ether groups, such as 2,2'-oxydisuccinic acid, or polyhydric alcohols partly or completely etherified with glycollic acid, or hydroxycarboxylic acids, for example tris-carboxymethyl glycerol, bis-carboxymethylglyceric acid and carboxymethylated or oxidized polysaccharides. Polymeric carboxylic acids with a molecular weight of at least 350 are also suitable in the form of their water-soluble sodium or potassium salts, for example polyacrylic acid, polymethacrylic acid, poly- $\alpha$ -hydroxyacrylic acid, polymaleic acid, polyitaconic acid, polymesaconic acid, polybutene tricarboxylic acid and the copolymers of the corresponding monomeric carboxylic acids with each other or with ethylenically unsaturated compounds such as ethylene, propylene, isobutylene, vinyl methyl ether or furan.

Complex forming polyphosphonic acid salts may also be present, e.g. the alkali metal salts of aminopolyposphonic acids, in particular aminotri-(methylenephosphonic acid), 1-hydroxyethane-1, 1-diphosphonic acid, phenylhydroxymethane diphosphonic acid, methylene diphosphonic acid and salts of the higher homologues of the above mentioned polyphosphonic acids. Mixtures of these complex formers may also be used.

The remaining constituents which may be present in the component (A) include greying inhibitors, optical clarifying agents, stabilizers such as magnesium silicate, brightening substances such as dyes, and additives which render the product more easily sprayable, e.g. alkali metal salts of toluene-, xylene- or cumenesulphonic acids.

- Suitable greying inhibitors include in particular carboxymethylcellulose and cellulose mixed ethers containing varying quantities of carboxymethyl, methyl and/or hydroxyethyl groups, water-soluble polyesters and polyamides of polybasic carboxylic acids and glycols or diamines which contain free carboxyl groups capable of salt formation, betaine groups or sulphobetaine groups, and colloidal, water-soluble polymers or copolymers of vinyl alcohol, vinyl pyrrolidone, acrylamide and acrylonitrile. Suitable optical clarifying agents include the alkali metal salts of 4,4-bis-(2''-anilino-4''-morpholino-1,3,5-triazinyl-6''-amino)-stilbene-2,2'-disulphonic acid and compounds which have a similar structure but contain a diethanolamino, methylamino or  $\beta$ -methoxyethylamino group instead of the morpholine group. Compounds of the type diacrylpyrazoline may also be used as clarifying agents for polyamide fibres, for example 1-(p-sulphonamidophenyl)-3-(p-chlorophenyl) $\Delta^2$ -pyrazoline and compounds with a similar structure which contain a carboxymethyl or acetylamino group instead of the sulphonamide group. Substituted aminocoumarines may also be used, e.g. 4-methyl-7-dimethylamino- or 4-methyl-7-diethylamino-coumarine. The compounds 1-(2-benzimidazolyl)-2-(1-hydroxyethyl-2-benzimidazolyl)-ethylene and 1-ethyl-3-phenyl-7-diethyl-amino-carbostyryl may also be used as polyamide clarifying agents. Suitable clarifying agents for polyester and polyamide fibres are the compounds 2,5-di-(2-benzoxazolyl)-thiophene, 2-(2-benzoxazolyl)-naphtho-[2,3-b]-thiophene and 1,2-di-(5-methyl-2-benzoxazolyl)-ethylene. Clarifying agents of the substituted diphenylstyryl type may also be present. Mixtures of the above mentioned clarifying agents may also be used.
- Components (B) contain the silicone in quantities of from 1 to 15% by weight, preferably from 2 to 10% by weight, and at least one carrier substance for the silicone. The silicones are preferably dimethylpolysiloxanes corresponding to the following formula



- in which n represents a number of from 20 to 2000. The silicones may in addition contain pyrogenic silicon dioxide (aerosil) as mixing constituent, in particular in quantities of from 5 to 20% by weight.
- Silanised silica, in particular finely divided trimethylsilanised  $\text{SiO}_2$ , is also a suitable additive. As is known, these additives increase the foam inhibiting action.
- The structural substances mentioned as constituents of component (A) may be used as carrier substance, in particular the polymer phosphates, carbonates, silicates, sulphates and aluminosilicates of sodium and possibly also magnesium silicate. Emulsifiers may also be present, for example, the non-ionic surface active agents mentioned as constituents of components (A) and (C), in particular ethoxylation products of higher molecular weight alcohols. Examples include alcohols which are either linear or methyl branched in the 2-position and have from 12 to 18 carbon atoms and from 10 to 30 ethylene glycol ether groups. Water-insoluble, waxy compounds such as ester waxes and/or hydrocarbon waxes may also be present. Emulsifiers and waxy compounds improve the distribution of silicone on the carrier material. The same effect may be obtained with water-soluble polymers such as cellulose ethers, polyglycols, polyvinyl alcohol, polyvinyl pyrrolidone, polyacrylates and polyacrylamides. Particular suitable cellulose ethers are sodium carboxymethylcellulose, methyl cellulose and hydroxyethyl- and hydroxypropylcellulose.
- The quantity in which the compounds mentioned above are present in component (B) may vary within the following limits:
- 1 to 15, preferably 2 to 10% by weight of silicone,
  - 50 to 99, preferably 60 to 90% by weight of carrier substance in particular sodium tripolyphosphate, sodium sulphate, sodium aluminosilicate and/or magnesium silicate,
  - 0 to 40, preferably 2 to 30% by weight of emulsifiers, in particular ethoxylated higher molecular weight alcohols,
  - 0 to 25, preferably 0 to 15% by weight of waxy compounds, and
  - 0 to 25, preferably 0 to 10% by weight of water-soluble polymers, in particular Na-carboxymethylcellulose.
- The preparation of components (B) may be carried out by granulating the carrier material such as anhydrous or partially hydrated sodium tripolyphosphate, anhydrous sodium sulphate or pulverulent aluminosilicate or magnesium silicate with a mixture of silicone, emulsifying agents and optionally other additives, which mixture has been melted by heating or liquefied by the addition of water. The usual granulating apparatus such as drum mixers, ploughshare mixers, cascade mixers or free falling mixers or granulating plates may be used, and granulation may be carried out batchwise or continuously. The granulate obtained is free from dust, free flowing and does not form lumps.
- The proportion of silicone in component (B) and the proportion of component (B) in the total mixture should preferably be such that the proportion of silicone amounts to from 0.2 to 1.6% by weight when powerful foaming agents are present and from 0.05 to 0.3% by weight when weak foaming agents are present (soaps, non-ionic surface active agents).

Component (C) preferably contains a per-compound as carrier substance, for example sodium percarbonate, most preferably sodium perborate. In materials which contain little or no bleach, the per-compound may be partly or completely replaced by the structural substances mentioned as constituents of component (A), for example a phosphate, polymer phosphate, silicate, carbonate or sulphate in the form of the alkali metal salt and in particular the sodium salt. However, the carrier substance contained in component (C) is preferably sodium perborate tetrahydrate.

The non-ionic active substance applied as a granulate to the carrier substance may consist of the non-ionic surface active agents mentioned as constituents of component (A) but it preferably consists of a mixture having the following composition:

- 10 C<sub>1</sub>) At least one ethoxylation product of a straight chain, saturated primary alcohol having 16 to 22 carbon atoms, which ethoxylation product contains from 3 to 7 glycol ether groups;
- C<sub>2</sub>) at least one ethoxylation product of the following compounds, which ethoxylation product contains from 5 to 15 glycol ether groups:
  - 15 (a) a straight chain or branched chain primary or secondary, saturated or mono-unsaturated alcohol in which the saturated hydrocarbons have from 10 to 15 carbon atoms and the unsaturated hydrocarbons from 10 to 18 carbon atoms,
  - (b) a straight chain, saturated vicinal diol having from 12 to 18 carbon atoms, and
  - (c) an alkyl phenol containing a straight chain alkyl group which has from 7 to 12 carbon atoms, in which the proportion by weight of (C<sub>1</sub>) to (C<sub>2</sub>) is in the range of from 2:3 to 5:1.
- 20 Examples of the compounds mentioned under (C<sub>1</sub>) include ethoxylation products of cetyl, stearyl, arachyl and behenyl alcohol and of linear primary C<sub>17</sub>—C<sub>21</sub> alcohols which have an odd number of carbon atoms, and mixtures of the aforesaid alcohols. Ethoxylated saturated tallow fatty alcohols containing an average of from 4 to 6 glycol ether groups are particularly suitable.
- The ethoxylation products mentioned under (C<sub>2</sub>) include the following:
  - 25 (a) Those of fatty alcohols of natural and synthetic origin. For example: Decanol, lauryl and myristyl alcohol and mixtures thereof, e.g. C<sub>10</sub>—C<sub>14</sub> fractions obtained from coconut or palm kernel fatty alcohols; synthetic primary alcohols such as undecanol, tridecanol or pentadecanol; C<sub>10</sub>—C<sub>15</sub> oxo alcohols, unsaturated fatty alcohols such as palmitoleyl alcohol and oleyl alcohol; secondary C<sub>10</sub>—C<sub>16</sub> alcohols in which the hydroxyl group may be in the 2-position or in any position or may be statistically distributed over the carbon chain; branch chained alcohols, e.g. guerbetyl alcohols, such as 2-butyl octanol and 2-pentyl nonanol, methyl-branched C<sub>10</sub>—C<sub>15</sub> alcohols or other primary or secondary branched C<sub>10</sub>—C<sub>15</sub> alcohols obtained from petroleum hydrocarbons, or mixtures of the above mentioned compounds;
  - 30 (b) those of vicinal diols, for example 1,2-diols, such as 1,2-dihydroxydodecane, 1,2-dihydroxytetradecane, 1,2-dihydroxyhexadecane, 1,2-dihydroxyoctadecane or 1,2-dihydroxyalkanes having 11, 13, 15 or 17 carbon atoms, or C<sub>10</sub>—C<sub>18</sub> diols having vicinal hydroxyl groups statistically distributed over the carbon chain;
  - (c) those of alkylphenols having a linear alkyl chain, e.g. octylphenol, nonylphenol and decylphenol and mixtures thereof.
- 40 Mixtures of ethoxylation products mentioned under (a) to (c) are also suitable. The degree of ethoxylation of the primary saturated alcohols and oxo alcohols mentioned under (a) is preferably from 5 to 15 and that of the other compounds preferably 5 to 12. It is preferred to use ethoxylation products of straight chain compounds.
- The proportion by weight of the substance mentioned under (C<sub>1</sub>) to the substance mentioned under (C<sub>2</sub>) is in the range from 5:1 to 2:3, preferably from 1:1 to 3:1. The two substances should form a homogenous mixture which is fused or agglomerated with perborate particles or forms a more or less complete coating over the perborate particles. The quantity of coating substance based on the quantity of sodium perborate should preferably be from 3 to 20% by weight, in particular from 5 to 15% by weight.
- 50 Component (C) is prepared by intimately mixing a fused mixture of components (C<sub>1</sub>) and (C<sub>2</sub>) which has been melted at temperatures above 35°C, preferably at 50 to 70°C, with the pulverulent to granular sodium perborate which may be at a temperature of from 0°C to 25°C. Additional heating of the powder during the mixing process is unnecessary since homogeneous distribution without formation of dust is ensured, when even a relatively cold powder is used.
- 55 As in the case of component (B), mixing may be carried out continuously or batchwise, using the usual mixing, granulating or spraying apparatus, e.g. drum, cascade or ploughshare mixers or any other mixers operated on the principle of forced circulation as well as arrangements in which the liquid melt is continuously sprayed on a free falling powder or on a powder which is spread in a thin layer on a conveyor belt. Spraying may be followed by regranulation if necessary.
- 60 The particle size and weight per litre of the sodium perborate used may vary within wide limits but the proportion of coarse particles measuring more than 2 mm should be less than 10% by weight, preferably less than 2% by weight.
- The proportion of very fine particles measuring less than 0.1 mm in component (C) and in component (B) is preferably less than 25% by weight, in particular less than 10% by weight. The average particle size is suitably from 0.1 to 0.8 mm.

Treatment with the liquid mixture generally results in an increase in the particle size, mainly by particles below 0.2 mm being substantially or completely agglomerated to form larger particles. The proportion of particles measuring from 1 to 3 mm increases only slightly. Even large particles may, if necessary, be screened out, reduced in size and then used again. The average particle size of components (B) and (C) is from 0.4 to 1.0 mm and thus of the same order as that of a washing powder obtained by spray drying. It is to be regarded as a particular advantage that this counteracts the undesirable process of separation into components during transport or storage of the detergent.

Other additives, such as dyes, pigments or perfume substances, may also be applied to the carrier material of component (B) and/or (C) if desired. Coloured additives may be used to give the powder mixture a speckled appearance which helps to identify it and makes it attractive in appearance.

The mixtures of powder components contain from 0.01 to 0.5 part by weight of component (B) and from 0.05 to 1 part by weight of component (C) to 1 part by weight of component (A). If the carrier substance used for the preparation of component (C) consists exclusively or predominantly of sodium perborate, the mixtures preferably contain from 0.1 to 0.5 parts by weight of (C) to 1 part by weight of (A). The proportion of non-ionic surface active agent in which the proportion of glycol groups to carbon atoms is in the range of from 1:3 to 1:6 should be from 1 to 10% by weight, preferably from 2 to 8% by weight of the mixture, and the proportion of silicone in the mixture should be from 0.02 to 1.6% by weight, preferably from 0.05 to 0.5% by weight.

Measuring out of the three components and subsequent mixing may be carried out in separate stages or simultaneously.

It is preferable to operate continuously, and automatic conveyor type weighers used in combination with free fall mixers have proved to be particularly suitable for this purpose. Additional mechanically operated mixing devices are not generally necessary. If they are used, it is advisable to handle the powder mixture carefully in order to avoid destruction of the hollow ball structure of the sprayed powder and an undesirable increase in the proportion of the fine particles and dust. If additional powder constituents such as enzymes or bleach activators are to be added to the powder, this may advantageously be done at the same time.

The powder mixtures prepared according to the invention are distinguished by their very advantageous washing-in characteristics, i.e. even in badly designed washing-in apparatus, they are completely washed from the detergent dispenser into the washing drum within the washing-in time set by the machine, without leaving any residue. On the one hand, it was surprising that the washing-in process was impaired if only a fraction of all the powder particles were treated with silicones, but it was not less surprising to find that it was by no means necessary to treat the whole quantity of powder with the non-ionic surface active agent in order to eliminate the troublesome wetting effect of silicone and that, on the contrary, a comparatively small proportion of component (C), measured against the total quantity of powder, was completely sufficient for this purpose. In addition, the method of preparation according to the invention substantially reduces the losses by vaporisation which particularly affect the low ethoxylated non-ionic surface active agents in the process of hot spray drying. The process is therefore also much to be preferred from an environmental point of view since it eliminates the contamination of the exhaust air from the hot spraying towers by vaporised non-ionic surface-active agent. Furthermore, the detergent compositions are distinguished by being substantially free from dust, stable in storage, freely pourable and reliable and uniform in their foaming characteristics. The well known and troublesome phenomenon that the action of a foam inhibitor is diminished or even destroyed if the inhibitor is incorporated in a detergent slurry and then sprayed is reduced or substantially obviated in the process according to the invention.

Although detergents which are obtained by mixing spray powders with a perborate granulate containing non-ionic surface active agents have been disclosed in German Auslegeschrift No. 2,418,294, these detergents do not contain silicone defoaming agents and therefore do not pose the problems due to unsatisfactory wetting and washing-in characteristics. The problems to be solved and the procedure are therefore do not pose the problems due to unsatisfactory wetting and washing-in characteristics. The problems to be solved and the procedure are therefore different from those of the present invention.

### Examples

In order to be able to examine more closely the washing in characteristics of samples of detergent under reproducible conditions similar to those encountered in practice, three detergent dispensers from different mass produced washing machines were used. The detergent was introduced through a powder funnel fixed over the centre of the dispenser and having an outlet aperture with an internal width of 30 mm. Each of the washing-in nozzles of the chambers was connected to the water supply (water temperature about 14°C) through a water meter, a magnetically operated rapid closure valve and a pressure reducing valve (restrictor valve). The washing-in time, quantity of water and water pressure could therefore be exactly adjusted and measured. The water pressure was set at 0.5 excess atmospheres in all the experiments. The quantity of detergent weighed-in was in each case 100 g and the quantity of water introduced was 10 litres. The time until washing-in was completed was checked and if any residue was formed, this was dried and weighed.

The results were assessed according to the following grades:

Grade 1: Complete washing-in with less than 5 litres,

Grade 2: complete washing-in with 5 to 10 litres,

Grade 3: less than 5 g residue,

5 Grade 4: 5 g to 20 g residue,

Grade 5: more than 20 g residue.

The experiments were repeated five times in each case and the results were averaged. Average grades of 1 and 2 indicate very good to good washing-in characteristics. Detergents assessed with Grade 3 are regarded as only just acceptable, provided none of the individual tests reached Grade 4 or

10 5.

The compositions of the spray dried detergent components (components A) in % by weight are entered in Table 1. These are compositions which foam very strongly because of their powerful foaming constituents or low soap content, particularly at temperatures above 70°C. They were prepared by spray drying a slurry (water content 37%) in a spray tower in which drying air was introduced at the bottom at a temperature of 290°C and exhaust air left at the top at a temperature of 97°C. The anionic surface active agents, structural salts and other salt-type compounds were used in the form of sodium salts. EO represents ethylene oxide fixed by chemical addition.

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Table 1

Constituent (in % by weight)	Example				
	1	2	3	4	5
n-Dodecylbenzene sulphonate	12.0	—	—	—	11.5
n-alkane sulphonate	—	11.0	—	—	—
C <sub>15</sub> —C <sub>18</sub> - $\alpha$ -olefine sulphonate	—	—	10.0	—	—
Tallow fatty alcohol sulphate	—	—	—	12.0	—
Soap (tallow:coconut=9:1)	2.2	2.0	2.5	1.5	—
Tallow alcohol+5 EO	2.0	2.5	2.0	2.0	—
Tallow alcohol+14 EO	1.9	3.2	3.2	3.0	—
Tripropylphosphate	60.0	60.0	30.0	30.0	10.0
Na-aluminosilicate	—	—	30.0	30.0	40.0
Na-silicate (Na <sub>2</sub> O:SiO <sub>2</sub> =1:3)	3.0	3.0	2.0	2.0	2.0
Mg silicate	2.1	2.1	2.1	1.1	2.1
EDTA	0.3	0.3	0.3	0.3	0.3
Carboxymethylcellulose	0.9	1.0	0.8	0.8	1.0
Optical clarifying agent	0.3	0.3	0.3	0.3	0.3
Sodium sulphate	7.1	7.5	3.5	4.5	9.5
Water	remainder	remainder	remainder	remainder	remainder

20 The compositions in % by weight of the components (B) which contain silicones are entered in Table 2.

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These components were prepared in a granulating drum into which the salts or salt mixtures (particle size 0.2 to 1 mm) used as carrier material were first introduced and the emulsion or solvent-free melt containing silicone was then added, and the mixture was granulated and homogenised. The

25 silicone used consisted of a dimethylpolysiloxane (average molecular weight 13000 to 14500) in

25

which silica was dispersed (arosil, average particle size 0.25 m $\mu$ ). The montan wax had a melting range of from 100 to 105°C.

Table 2

<i>Liquid mixture</i>	<i>Example</i>		
	<i>1—3</i>	<i>4</i>	<i>5</i>
Silicone	3.7	5.6	5.3
SiO <sub>2</sub>	0.3	0.4	0.4
Tallow alcohol+14 EO	—	6.0	—
Tallow alcohol+25 EO	26.0	—	16.0
Montan wax	—	—	11.0
Carboxymethylcellulose	—	0.2	—
Water	—	9.0	—
Carrier substance			
Sodium tripolyphosphate	70.0	—	67.3
Sodium sulphate	—	68.8	—
Magnesium silicate	—	10.0	—

5 The sodium perborate tetrahydrate found to have the following composition by screen analysis: 5

Mesh width (mm):	1.6	0.8	0.4	0.2	0.1	<0.1
Percent by weight	0	1.5	38	44.5	12	4

was used for the preparation of component (C) in Examples 1 to 4.

The granulate in Example 5 was prepared on the basis of sodium tripolyphosphate.

10 The perborate or tripolyphosphate was introduced into a drum mixer equipped with mixing 10  
elements rotating at high speed (so-called LÖDIGE mixer). The non-ionic surface active mixtures having the composition shown in Table 3 were introduced into the rotating mixer. The temperature of the fused active mixtures was 60°C. Mixing was terminated after 3 minutes, when the granulates formed were found to be homogenous, free from dust and pourable.



Table 3

Example	Binary surface active mixture (Quantities in % by weight)	First component in apparatus (in % by weight)
1	(C <sub>1</sub> ) 7.5 Tallow alcohol+5 EO (C <sub>16</sub> :C <sub>18</sub> alcohol=1:1)	90 Na perborate
2 and 3	(C <sub>2</sub> ) 2.5 oleyl alcohol+5 EO (C <sub>1</sub> ) 5 Tallow alcohol+5 EO (C <sub>16</sub> :C <sub>18</sub> alcohol=1:1)	90 Na perborate
4	(C <sub>2</sub> ) 5 Oleyl alcohol+5 EO (C <sub>1</sub> ) 5 Tallow alcohol+5 EO (C <sub>16</sub> :C <sub>18</sub> alkyl=1:2)	90 Na perborate
5	(C <sub>1</sub> ) 10 Tallow alcohol+5 EO (C <sub>16</sub> :C <sub>18</sub> alkyl=1:2) (C <sub>2</sub> ) 5 C <sub>12-15</sub> -oxo alcohol+7 EO	85 Na tripolyphosphate

The proportions of components (A), (B) and (C) in the mixture and the resulting proportion of silicone defoaming agent and of tallow alcohol+5 EO (=component C<sub>1</sub>) in the mixtures and in the end product are shown in Table 4.

Table 4

Example	A	Parts by weight B	C	% by weight silicone	% by weight C <sub>1</sub>
1	1	0.1	0.15	0.3	2.7
2	1	0.2	0.3	0.5	2.3
3	1	0.2	0.3	0.5	2.7
4	1	0.1	0.3	0.4	2.1
5	1	0.14	0.36	0.5	2.4

In a series of comparison experiments, using the same proportions and other experimental conditions, the non-ionic surface active agents C<sub>1</sub> and C<sub>2</sub> were also sprayed as a constituent of component (A) and the powder obtained from the spray tower was mixed with equal parts of silicone-containing premix and unpretreated perborate (according to Examples 1 to 4) or tripolyphosphate (according to Example 5). The results of the washing-in test are entered in Table 5. They confirm the superiority of the procedure according to the invention.

Table 5

Example	Experiment	Assessment Comparison Experiment
1	1—2	3—4
2	1—2	3—4
3	1—2	3—4
4	1—2	3—4
5	1	3—4

The advantageous washing-in characteristics were confirmed in practical use. Furthermore, when used in automatic washing machines with horizontal drum containing lightly soiled laundry, the detergents were found to be proof against overfoaming at concentrations from 3 to 8 g/l.

#### Claims

- 5 1. A process for the preparation of a pulverulent detergent with improved solution properties containing an organic silicon polymer as foam inhibitor, in which
  - A) 1 Part by weight of a powder which has been spray dried using hot gases and which is free from organic silicon polymers and per-compounds and contains the following components:
    - 5 to 30% by weight of at least one anionic and/or non-ionic active substance,
    - 10 50 to 94% by weight of at least one structural substance which is a phosphate, polyphosphate, silicate, aluminosilicate, carbonate, sulphate, polycarboxylate or phosphonate in alkali metal salt form, and
    - 1 to 20% by weight of other conventional detergent constituents,
    - B) 0.01 to 0.5 parts by weight of a pulverulent or granular premix prepared by granulating one or more of the structural substances specified under (A) and/or magnesium silicate with 1 to 15% by weight, based on the premix, of organic silicon polymers, and
    - 15 C) 0.05 to 1 part by weight of another pulverulent or granular premix prepared by granulating a pulverulent pre-compound and/or one or more of the structural substances specified under (A) with 3 to 25% by weight, based on the weight of the premix, of at least one non-ionic active substance which contains polyglycol ether groups and of which at least 40% by weight consists of a compound having
      - 20 from 12 to 22 carbon atoms in the hydrophobic residue and in which the proportion of the number of ethylene glycol ether groups to the number of carbon atoms in the hydrophobic residue is from 1:3 to 1:6 are mixed together so that the organic silicon polymer contained in component (B) amounts to from 0.05 to 1.6% by weight of the total quantity of the mixture and the non-ionic active substance
        - 25 which has the proportion of from 1:3 to 1:6 in component (C) amounts to from 1 to 10% by weight of the total mixture.
  2. A process as claimed in claim 1, in which component (B) is prepared by granulating in known manner 60 to 90% by weight of at least one pulverulent to granular carrier substance consisting of sodium tripolyphosphate, sodium sulphate, sodium aluminosilicate or magnesium silicate with a
    - 30 mixture which may contain water and which consists of
      - 2 to 10% by weight of silicone polymers,
      - 2 to 30% by weight of emulsifiers from the class of ethoxylated higher molecular weight alcohols,
      - 0 to 15% by weight of water-insoluble waxes, and
      - 0 to 10% by weight of water-soluble polymers, in particular cellulose ethers.
  3. A process as claimed in claim 1, in which the substance used as component (C) is a granular premix which has been prepared by the granulation of sodium perborate with from 3 to 20% by weight of a mixture having the following composition:
    - (C<sub>1</sub>) an ethoxylation product of a straight chain, saturated primary alcohol which has from 16 to 22 carbon atoms, which ethoxylation product has at least 3 to 7 glycol ether groups,
    - 40 (C<sub>2</sub>) at least one ethoxylation product of the following compounds, which ethoxylation product has from 5 to 15 glycol ether groups:
      - a) a straight chain or branched chain primary or secondary, saturated or mono-unsaturated alcohol in which the saturated hydrocarbons have from 10 to 15 carbon atoms and the unsaturated hydrocarbons from 10 to 18 carbon atoms,
      - 45 b) a straight chain, saturated vicinal diol having from 12 to 18 carbon atoms, and
      - c) an alkyl phenol having a straight chain alkyl group with from 7 to 12 carbon atoms,
    - in which the proportion by weight of (C<sub>1</sub>) to (C<sub>2</sub>) is from 5:1 to 2:3.
    4. A process as claimed in claim 1 or claim 2, in which 1 part by weight of component (A) is mixed with from 0.05 to 0.3 parts by weight of component (B) and from 0.1 to 0.5 parts by weight of component (C) so that the total quantity of organic silicon polymer in the mixture is from 0.1 to 0.5% by weight and the total quantity of non-ionic surface active agent (C<sub>1</sub>) is from 2 to 8% by weight.
    5. A process as claimed in claim 1 substantially as herein described with reference to any of the Examples.
    6. A detergent with improved solution properties which consists of a mixture of the following
      - 55 powder components (A), (B) and (C):
        - a) 1 part by weight of a spray dried powder which is free from per compounds and contains:
          - 5 to 30% by weight of at least one anionic and/or non-ionic active substance,
          - 50 50 to 94% by weight of at least one structural substance which is a phosphate, polyphosphate, silicate, aluminosilicate, carbonate, sulphate, polycarboxylate, or phosphonate in alkali metal salt form, and
          - 60 1 to 20% by weight of another conventional detergent constituent,
          - b) 0.01 to 0.5 parts by weight of a pulverulent or granular premix prepared by granulating one or more of the structural substances mentioned under (A) and/or magnesium silicate with from 1 to 15% by weight, based on the premix, of organic silicon polymers, and

- c) 0.05 to 1 part by weight of a pulverulent or granular premix consisting of a pulverulent per-compound and/or one or more of the structural substances mentioned under (A), and  
 3 to 25% by weight, based on the weight of the premix, of at least one non-ionic active substance which is fused or agglomerated with the premix and which contains polyglycol ether groups and at least 40% by weight of which consists of a compound which has from 12 to 22 carbon atoms in the hydrophobic residue and in which the proportion of the number of carbon atoms in the hydrophobic residue is in the range of from 1:3 to 1:6,  
 wherein the total quantity of organic silicon polymers in the detergent is from 0.02 to 1.6% by weight and the total quantity of non-ionic active substance which has the ratio of from 1:3 to 1:6 is 1 to 10% by weight.
7. A detergent as claimed in claim 6 in which component (B) consists of a granular premix which is composed of:  
 60 to 90% by weight of at least one of the following carrier substances: Sodium tripolyphosphate, sodium sulphate, sodium aluminosilicate and magnesium silicate and a mixture of the following composition which is fused or agglomerated with said premix:  
 2 to 10% by weight of silicone polymers,  
 2 to 30% by weight of emulsifiers from the class of ethoxylated higher molecular weight alcohols,  
 0 to 15% by weight of water-insoluble waxes, and  
 0 to 10% by weight of water-soluble polymers, in particular cellulose ethers.
8. A detergent as claimed in claim 6 or claim 7, in which component (C) consists of a granular premix which is composed of from 80 to 95% by weight of sodium perborate and from 3 to 20% by weight of a mixture of non-ionic active substances which is fused or agglomerated with said premix and which has the following composition:  
 (C<sub>1</sub>) an ethoxylation product of a straight chain, saturated primary alcohol having from 16 to 22 carbon atoms, which ethoxylation product has from 3 to 7 glycol ether groups,  
 (C<sub>2</sub>) at least one ethoxylation product of the following compounds, which ethoxylation product has from 5 to 15 glycol ether groups:  
 a) a straight or branched chain, primary or secondary saturated or mono-unsaturated alcohol in which the saturated hydrocarbons have from 10 to 15 carbon atoms and the unsaturated hydrocarbons have from 10 to 18 carbon atoms,  
 b) a straight chain, saturated vicinal diol having from 12 to 18 carbon atoms, and  
 c) an alkyl phenol containing a straight chain alkyl group which has from 7 to 12 carbon atoms, in which the proportion by weight of (C<sub>1</sub>) to (C<sub>2</sub>) is in the range of from 5:1 to 2:3.
9. A detergent as claimed in any of claims 6 to 8 which consists of a homogeneous mixture of 1 part by weight of component (A), 0.05 to 0.3 parts by weight of component (B) and 0.01 to 0.5 parts by weight of component (C) such that the total quantity of organic silicon polymer in the mixture is from 0.05 to 0.5% by weight and the total quantity of non-ionic surface active agent (C<sub>1</sub>) in the mixture is 2 to 8% by weight.
10. A detergent as claimed in claim 6 substantially as herein described with reference to the following Examples.
11. A detergent as claimed in any of claims 6 to 10 when prepared by a process as claimed in any of claims 1 to 5.